ASM Sc. J., 11, Special Issue 3, 2018 for SANREM, 66-73

Distribution of Heavy Metals (Cr, Mn, Fe, Co & Ni) in Marine Sediment Cores at Marudu Bay, Sabah

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A total of 70 sediment samples were collected from 9 sediment cores from Marudu Bay, Kudat. The main objective of this research was to identify the distribution of heavy metals namely Fe, Mn, Cr, Ni and Co in shallow water sediment and to identify the cause for such concentration of the heavy metals. Geologically, the study area in Marudu Bay consists of various type of rocks namely ultrabasic, basic and chert of ophiolite sequence; and sedimentary rock of Kudat Formation. The physico-chemical analysis conducted includes of pH value, organic matter percentage (OM%) and particle size distribution (PSD). The heavy metals were measured using ICP-OES instrument. The result of chemical analysis shows that Fe has the highest concentration followed by Mn, Cr, Ni and Co. The concentration of Fe is between 14680 mg/kg - 92341 mg/kg. For Mn, Cr, Ni and Co, the concentration range between 3.98 mg/kg - 11.76 mg/kg, 2.42 mg/kg - 3.35 mg/kg, 1.52 mg/kg - 2.22 mg/kg and 0.17 mg/kg - 0.37 mg/kg respectively. However, the distribution does not exceed the reference value. It is found that the heavy metals concentrations mostly influenced by the weathering of sedimentary rocks and there is no significant influence by the weathered mafic and ultramafic rocks of ophiolite sequence.

Keywords: Weathering, heavy metals, shallow marine, sediment core, Marudu Bay.

I. INTRODUCTION

The study of heavy metals distribution around estuaries and waters in Malaysia especially at Northern Sabah is still considered as insufficient and needed to be taken more seriously. At Peninsular Kudat, the occurrence of several different formations especially ophiolite complex and sedimentary rock has played a big role on the concentration of heavy metals in Marudu Bay in addition with continuous natural process and anthropogenic activities around shallow marine environment.

The Peninsular Kudat generally consists of Early Miocene sedimentary formation which is the Kudat Formation (Stephens, 1956; Tongkul, 2008). This formation can be divided to 2 dominant members which are the clastic sediment layers of Tajau Member and the Sikuati Member which is also sedimentary layer with addition of foraminatic limestone lenses (Clement & Keij, 1958). This sedimentary layer is underlain by the ophiolitic basement which can be found exposed on the south of Peninsular Kudat as well as several places around Sabah such as Kota Marudu – Pitas and Telupid (Graves *et al.*, 2000; Sahibin *et al.,* 1995). According to Sanudin & Baba (2007), ophiolitic basement is

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the oldest rock unit building up Sabah and often associated with oceanic crust including peridotite, serpentinite, spilite, pillow lava, basalt and diabase (Basir, 1992; Clement & Keij, 1958; Hutchison, 2005; Junaidi & Basir, 2012; Shariff *et al.*, 1992). The muddy and loose sediment deposits indicated that the area was topped with Quaternary Alluvium where most of the environment consists of mangrove trees. Therefore, the main objective of this study is to measured the concentration of heavy metals in shallow marine sediment and to identify the factor that control the distribution of these heavy metals.

II. MATERIALS AND METHOD

A. Study Location and Technique of Sampling

The study area is located on the offshore of Marudu Bay near Kudat Town (Figure 1). The research was conducted at a transition area that is the downstream of Karang River and is connected to Marudu Bay at the Kudat Peninsular. A total of 9 stations (named as SK1 to SK9) chosen for marine sediment sampling which were lined up into 3 lines, and each line consist of 3 stations separated around 100 m - 400 m (Figure 1). The samples were collected using Sediment Core Sampler where it was attached with a PVC pipe with diameter around 10 cm and length 50 cm or 1 m used to grab the sediment core and was sealed using cork and plastic for preservation.

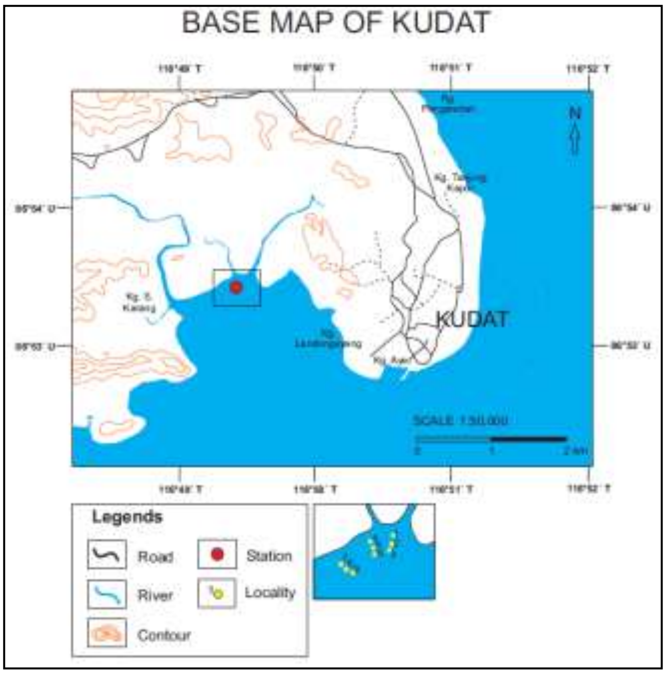

Figure 1. Base map of Kudat Town and the location for the marine sediment collection.

B. Experimental

The thickness of sediment cores samples were measured and cut into 2 cm thickness each and stored in sealed bags. A total of 70 samples were selected which represented the changes of lithologies in each core. All samples were analysis for the physico-chemistry properties and followed BS 1990. The parameter includes soil pH (BS 1337: 1990, Test 11 (A)), organic matter content (BS 1377: Part 3 (4.3): 1990) and particle size distribution (BS 1377: 1990, Test 7). The concentrations of heavy metals were measured using ICP-OES instrument.

Core Sample	Coordinates	pH	OM (%)	Soil Classification
SK1	N 06°53.445′ E 116°49.630′	5.53 - 7.45	3.82 - 9.38	Sandy loam & Loamy sand
SK2	N 06°53.409′ E 116°49.624′	6.72 - 7.47	4.31 - 9.47	Sandy loam
SK3	N 06°53.387′ E 116°49.619′	6.59 - 7.50	4.18 - 8.46	Sandy clay loam, Loamy sand & Sandy loam
SK4	N 06°53.423′ E 116°49.545′	5.83 - 6.41	3.77 - 6.61	Loamy sand & Sandy loam
SK5	N 06°53.397′ E 116°49.558′	5.24 - 6.05	6.41 - 10.66	Sandy loam & Sandy clay loam
SK6	N 06°53.379′ E 116°49.566′	5.29 - 6.56	5.44 - 12.93	Sandy loam & Sandy clay loam
SK7	N 06°53.331′ E 116°49.448′	7.27 - 7.56	1.41 - 2.18	Loamy sand & Sandy loam
SK8	N 06°53.313′ E 116°49.470′	7.13 - 7.45	2.12 - 10.15	Sandy loam
SK9	N 06°53.299′ E 116°49.492′	6.93 - 7.36	3.90 - 8.13	Sandy loam

The method of analysis as follows; 1.0 gm of clay-sized particle was prepared and well mixed with 14 ml *aqua regia* (HCl added with HNO_3 in 3:1 ratio) before left to react for a night. The solution were added with another 4 ml *aqua regia* and heated on hot plate, it was then filtered using Whatman 541 filter paper. The samples were stored under 4°C for preservation before analyzed.

III. RESULTS AND DISCUSSION

A. pH, organic matter and particle size distribution

Overall, the pH values of core SK1 were in between 5.53-7.45. For SK2, SK3, SK4 and SK5, each have pH values in the range of 6.72-7.47, 6.59-7.50, 5.83-6.41, and 5.24-6.05 respectively. SK6 and SK7 showed pH values around 5.29-6.56 and 7.27-7.56. Meanwhile, the pH values for SK8 and SK9 were between 7.13-7.45 and 6.93-7.36 each (Table 1).

For the organic matter (OM%) in sediment samples, SK1 and SK2 have the percentages between range 3.82%-9.38% and 4.31%-9.47%. SK3 has the range of 4.18%-8.46%, 3.77%-6.61% for SK4 while 6.41%-10.66% for SK5. SK6 has the highest percentage of 12.93% and SK7 recorded the lowest percentages which were 1.41%-2.18%. Sample SK8 and SK9 both have the range between 2.12%-10.15% and 3.90%-8.13% (Table 1).

The results for the particle size distribution showed that most of the samples were categorized as sandy loam, loamy sand and sandy clay loam (Table 1). The classifications were based on the soil texture classification triangle from United State of Department Agriculture (USDA, 1975). The classification is influenced by the depth of water and also distance from the shore where percentage of smaller particles is higher in deeper depth (Zhang et al. 2014). This shows that the sand textures mostly contributed by the parents rock of sandstone from Kudat Formation.

B. Heavy metals concentration

The range and average concentration of heavy metals in each core are presented in Table 2. In Figure 2, the graph of heavy metals concentration against depth in every core is plotted. From Table 2, SK9 has the highest average value for Fe (92341.22 mg/kg) and Mn (11.76 mg/kg). Cr is highest in SK2 (3.35 mg/kg) while SK6 has highest Ni (2.22 mg/kg) and also Co (0.37 mg/kg). The figure also showed a relatively high concentration of Fe compare to the other metals then followed by Mn, Cr, Ni and Co.

Meanwhile, Ni and Cr showed the same pattern and also similar range in the concentration of heavy metals. Co has the lowest concentration range and average (<1.00 mg/kg) in all cores except in SK6

sample (0.37 mg/kg). However, all the average concentrations obtained are below the reference values in earth crust and sedimentary rocks except for Fe. This can be caused by the presence the nearest parent rock of Kudat Formation. The appearance of ophiolite complex especially mafic and ultramafic rocks like serpentinites, peridotite, basalt and pillow lava do not influence the concentration of heavy metals in marine sediment in the study area. The sediment samples contain high amount of Fe due to oxidation of rock forming minerals in the parent rock (Baba & Mohamad, 1995).

Other than Fe, several previous studies had stated that igneous rock has potential to release heavy metals such as Cu, Cr, Co, Ni and Mn due to the chemical weathering processes (Al-Rousan *et al.*, 2016; Baba & Sanudin, 2007; Sahibin *et al.*, 1995; Tashakor *et al.*, 2014). Natural transportation process will carry these elements through rivers into lowland area or beach in form of suspended particles and also through air as atmospheric dust into the ocean thus contributing to a high concentration (Takematsu, 1992). However in the study area the presence of mangrove trees and swamp area at downstream of Sg. Karang Kudat, has helped in preventing most of the eroded particles and heavy metals to reach the bay. In marine sediments, the deposited elements will either adsorb to form lattice structure of minerals or stayed as free metal ions (Zhang *et al.*, 2014). Mangrove areas and plants that trap clay minerals will naturally become a sink for heavy metals due to their physical and chemical properties was reported by Merchand *et al.* (2006).

Generally, the distribution of heavy metals varies in each cores where it increases as it grows farther from the shore notably for Mn, Co and Fe (Fig 2 (c), (f), (i)). This is due to much longer time for adsorption and coagulation process to take place before particle settlement on the sea floor (Zal U'Yun *et al.,* 2010).

The similar pattern between Fe and Mn along the core might indicate the formation of Fe-Mn oxides as coating on sedimentary components such as biogenic silica and silicate minerals in oxic surroundings (Balachandran *et al.*, 2006; Tashakor *et al.*, 2014). Meanwhile, the distribution of Ni and Cr can be caused by the percentage of organic matter and clay minerals as both show slightly corresponding pattern (Ho *et al.*, 2010).

IV. SUMMARY

The result of chemical analysis shows that Fe has the highest concentration followed by Mn, Cr, Ni and Co. The average concentration of Fe is between 14680 mg/kg - 92341 mg/kg. For Mn, Cr, Ni and Co, the concentration range between 3.98 mg/kg - 11.76 mg/kg, 2.42 mg/kg - 3.35 mg/kg, 1.52 mg/kg - 2.22 mg/kg and 0.17 mg/kg - 0.37 mg/kg respectively. The distribution is controlled by the percentage of organic matter, fine-grained particles and also the distance from shore. The analysis also showed that concentration increase with increasing distance from the land. In conclusion, the heavy metals concentrations in marine sediments around Marudu Bay of Sg Karang, mostly influenced by the weathering of sedimentary rocks and there is no significant influence of heavy metals from the weathered of igneous rock of ophiolite sequence.

V. ACKNOWLEDGMENT

This research was supported in part by Malaysian Institute of Nuclear Agency under Grant No. GL00147. All laboratory work has been done in the Laboratory of Faculty Science and Natural Resources, Universiti Malaysia Sabah.

Table 2. Value in each core with reference material (*Vinogradov (1966); **Taylor & McLennan (1985 and 1995)).

	Cr (mg/kg)		Mn (mg/kg)		Fe (mg/kg)		Co (mg/kg)		Ni (mg/kg)	
Sample	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
SK1	1.57 - 4.77	2.74	3.57 - 5.98	4.93	9286 - 61912	19855.57	0.11 - 0.27	0.18	1.05 - 2.98	1.72
SK2	1.84 - 9.88	3.35	2.62 - 10.30	6.04	3924 - 66061	19288.69	0.04 - 0.37	0.21	1.15 - 4.93	1.95
SK3	1.42 - 3.96	2.43	2.19 - 7.83	5.82	4545 - 57167	35737.19	0.04 - 0.32	0.18	1.19 - 2.04	1.57
SK4	1.91 - 6.38	3.26	2.47 - 4.98	3.98	4001 - 18005	14680.94	0.08 - 0.35	0.18	1.31 - 2.73	1.82
SK5	2.46 - 3.72	2.97	3.27 - 10.26	6.28	39761 - 53468	47196.82	0.22 - 0.42	0.34	1.80 - 2.37	2.18
SK6	2.34 - 4.51	3.03	4.47 - 10.23	7.10	17106 - 76334	51675.84	0.19 - 0.49	0.37	1.59 - 3.00	2.22
SK7	2.01 - 2.97	2.42	3.76 - 10.08	6.21	10046 - 153515	51519.65	0.10 - 0.25	0.17	1.24 - 1.95	1.52
SK8	2.03 - 3.46	2.55	4.88 - 10.94	7.95	78435 - 15987	54754.64	0.18 - 0.34	0.27	1.42 - 2.09	1.79
SK9	2.50 - 3.75	3.01	7.62 - 14.47	11.76	52509 - 235869	92341.22	0.28 - 0.43	0.35	1.76 - 2.73	2.21
Sedimentary rock (clay & claystone)*	-	100	-	700	-	33300	-	20	-	95
Upper continental crust**	-	85	-	500	-	34900	-	17	-	44
Average continental crust**	-	185	-	1400	-	70800	-	24	-	105

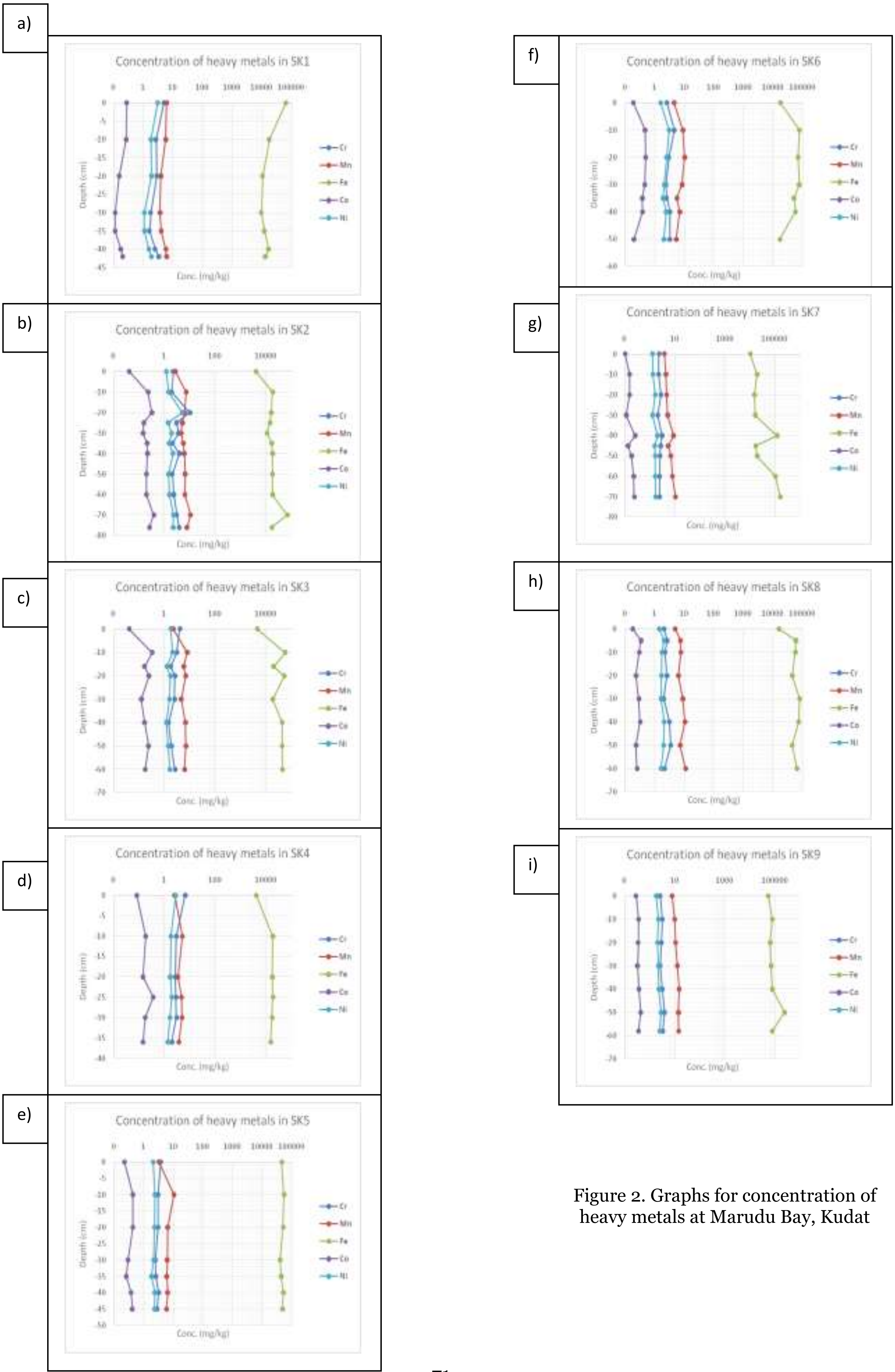

Figure 2. Graphs for concentration of heavy metals at Marudu Bay, Kudat

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